Generalized Elliott-Yafet theory of electron spin relaxation in metals: the origin of the anomalous electron spin life-time in MgB_2

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The temperature dependence of the electron spin relaxation time in MgB_2 is anomalous as it does not follow the temperature dependence of the resistivity above 150 K, it has a maximum around 400 K, and it decreases for higher temperatures. This violates the well established Elliot-Yafet theory of electron spin relaxation in metals. We show that the anomaly occurs when the quasiparticle scattering rate (in energy units) becomes comparable to the energy difference between the conduction- and a neighboring band. We find that the anomalous behavior is related to the unique band structure of MgB_2 and the large electron-phonon coupling. The saturating spin-lattice relaxation can be regarded as the spin transport analogue of the Ioffe-Regel criterion of electron transport.

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Knowledge of the electron spin-lattice relaxation time, T_1, of conduction electrons plays a central role in assessing the applicability of metals for information processing using electron spins, spintronics [1]. T_1 is the time it takes for the conduction electron spin ensemble to relax to its thermal equilibrium magnetization after a non-equilibrium magnetization has been induced e.g. by conduction electron-spin resonance (CESR) excitation [2] or by a spin-polarized current [1]. The Elliott-Yafet (EY) theory of T_1 in metals [3, 4] has been well established in the past 50 years on various systems such as elemental metals [5], strongly correlated one-dimensional [6], and some of the alkali fulleride salt [7] metals. It is based on the fact that the spin part of the conduction electron wave functions is not a pure Zeeman state but is an admixture of the spin up and down states due to spin-orbit (SO) coupling. As a result, momentum scattering due to phonons or impurities induces electron spin-flip, which leads to spin relaxation. Typically every millionth momentum scattering is accompanied by the electron spin-flip due to the relative weakness of the SO coupling. Thus, $T_1 \gg \tau$ (τ being the momentum relaxation time) which explains the motivation behind the efforts devoted to the spintronics applications of metals.

A consequence of the EY theory is the so-called Elliott-relation, i.e. a proportionality between T_1 and τ [3]:

$$\frac{1}{T_1} = \alpha \left(\frac{L}{\Delta E}\right)^2 \frac{1}{\tau} \qquad (1)$$

Here α is a band structure dependent constant and for most elemental metals $\alpha \approx 1..10$ (Ref. [5]). L is the SO splitting for spin up and down electrons in a valence (or unoccupied) band near the conduction band with an energy separation of ΔE. E.g. in sodium, the conduction band is $3s$ derived and the relevant SO state is the $2p$ with $\Delta E = 30.6$ eV and $L = 0.16$ eV giving $(L/\Delta E)^2 = 2.7 \cdot 10^{-5}$ [4].

The Elliott-relation shows that the temperature dependent resistivity and CESR line-width are proportional, the two being proportional to the inverse of τ and T_1, respectively. This enabled to test experimentally its validity for the above mentioned range of metals. Much as the Elliott-relation has been confirmed, it is violated in MgB_2 as therein the CESR line-width and the resistivity are not proportional above 150 K [8].

Here, we study this anomaly using MgB_2 samples with different B isotopes and impurity concentrations and we show that the anomalous effect is indeed intrinsic to MgB_2. We explain the anomaly with an exact treatment of the SO scattering of conduction electrons in the presence of a nearby band with energy separation ΔE, by extending the Mori-Kawasaki formula developed for localized spins to itinerant electrons. The result shows that the Elliott-relation breaks down when ΔE is comparable to $\hbar/\tau$. Adrian deduced a similar result with a qualitative argument [9].

The role of ΔE is disregarded in the EY theory since typical values are $\Delta E \approx 10$ eV and $\hbar/\tau = 2\pi k_B T \lambda \approx 6$ meV at $T = 100$ K and $\lambda = 0.1$ electron-phonon coupling. We show that the occurrence of the anomaly in MgB_2 is related to the unique features in its band structure and the large electron-phonon coupling.

We performed CESR measurements on three kinds of fine powder MgB_2 with isotope pure ^{10}B, ^{11}B, and natural boron (20 % ^{10}B and 80 % ^{11}B). The samples have

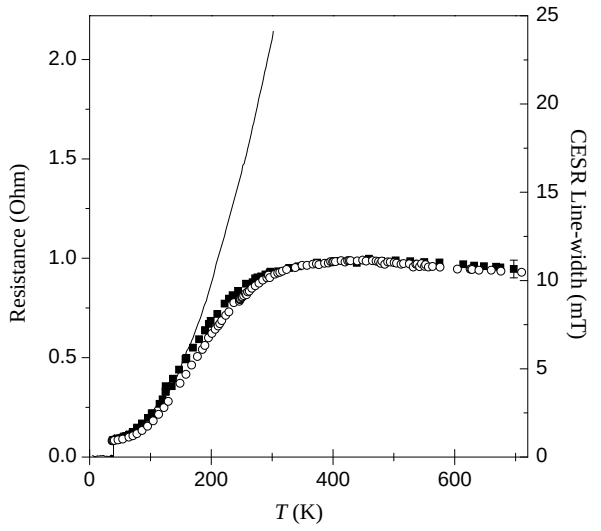

FIG. 1: Comparison of the temperature dependent CESR line-width (■: $Mg^{11}B_2$, ◯:MgB_2 of natural boron) and the resistance (solid curve) for $Mg^{11}B_2$. The two types of data overlap in the 40-150 K temperature range. A representative error bar is shown.

slightly different impurity content, shown by the varying residual CESR line-width, ΔB_0. The temperature dependent T_1 and the CESR line-width, ΔB, are related: $\Delta B = \Delta B_0 + 1/\gamma T_1$, where $\gamma/2\pi = 28$ GHz/T is the electron gyromagnetic factor. ESR spectroscopy was done on a Bruker X-band spectrometer (center field 0.33 T) in the 4-700 K temperature range on samples sealed under He in quartz tubes. The most important result of the current report, the anomalous temperature dependence of ΔB or T_1, is independent of sample morphology, isotope content, or thermal history. ΔB is also independent of the magnetic field, apart from a small change in ΔB_0 [10]. Resistance on pellet samples and SQUID magnetometry were studied on the same batch as those used for ESR. The $RRR > 20$ and the sharp (< 0.5 K) superconducting transition attest the high quality of the samples. Heating the samples in the ESR measurement (about 1 h duration) to 700 K does not affect the superconducting properties as shown by magnetization measurements.

We reported previously the anomalous temperature dependence of the CESR line-width in $Mg^{11}B_2$: although the line-width follows the resistance for the 40-150 K temperature range, it deviates above 150 K and saturates above 400 K [8]. This was confirmed independently [11, 12]. To our knowledge, this is the only known metal where such phenomenon is observed. We extended the previous measurement to 700 K and the result is shown in Fig. 1. Interestingly, the CESR line-width does not just saturate at high temperatures, as found previously, but *decreases* slightly above 500 K. The result is reversible upon cooling with no dependence on the thermal treatment protocol. The phenomenon is reproduced on several samples of different purity and boron isotopes, thus it is intrinsic to MgB_2.

We explain the anomalous temperature dependence of T_1 in general before including the specifics of MgB_2. The Elliott-Yafet theory disregards the magnitude of τ and takes life-time effects only to lowest order into account [3, 4]. The extended description involves the Kubo-formalism and is based on a two-band model Hamiltonian, $H = H_0 + H_{\rm SO}$, where:

$$H_0 = \sum_{k,\nu,s} \left[\epsilon_\nu(k) + \hbar\gamma B s\right] c^+_{k,\nu,s} c_{k,\nu,s} + H_{\rm scatt}, \qquad H_{\rm SO} = \sum_{k,\nu\neq\nu',s,s'} L_{s,s'}(k) c^+_{k,\nu,s} c_{k,\nu',s'} \tag{2}$$

Here $\nu, \nu' = 1$ or 2 are the band, s, s' are spin indices, $L_{s,s'}$ is the SO coupling, and B is the magnetic field along the z direction. $H_{\rm scatt}$ is responsible for the finite τ. The SO coupling does not split spin up and down states in the same band for a crystal with inversion symmetry, however it joins different spin states in the two bands [1]. The Hamiltonian in Eq. 2 is essentially the same as that considered by Elliott [3]. However, instead of a time-dependent perturbation treatment, we calculate T_1 from the Mori-Kawasaki formula [13, 14]:

$$\frac{1}{T_1} = -\frac{1}{2\chi_0 B} {\rm Im} G^R_{PP^+}(\omega_{\rm L}), \tag{3}$$

where χ_0 is the static magnetic susceptibility, $\omega_{\rm L} = \gamma B$ is the Larmor frequency, and $G^R_{PP^+}(\omega)$ is the Fourier transform of

$$G^R_{PP^+}(t) = -i\Theta(t)\langle[P(t), P^+(0)]\rangle_{H_0}, \qquad P = [H_{\rm SO}, S^+]. \tag{4}$$

The expectation value in Eq. 4. is evaluated with the unperturbed Hamiltonian, H_0.

Assuming that the two bands are separated by $\Delta E(k) = \epsilon_1(k) - \epsilon_2(k) = \hbar\Delta\omega(k)$, a standard calculation yields [15]:

$$\frac{1}{T_1} = \left\langle \frac{L_z^2(k_F) + 2|L_{\downarrow,\uparrow}(k_F)|^2}{\hbar^2} \frac{\tau}{1 + (\Delta\omega(k_F)\tau)^2} \right\rangle, \tag{5}$$

where the $\langle \dots \rangle$ means Fermi surface averaging, $L_z(k) = L_{\uparrow,\uparrow}(k) - L_{\downarrow,\downarrow}(k)$, and we neglected $\omega_{\rm L}$, which is small compared to $\Delta\omega(k_F)$. Eq. 5. was previously deduced by Adrian using a qualitative argument, which involved an effective magnetic field, $L/\hbar\gamma$, fluctuating with τ correlation time due to the SO coupling [9].

We approximate Eq. 5 using effective values for the band-band energy separation and the SO coupling:

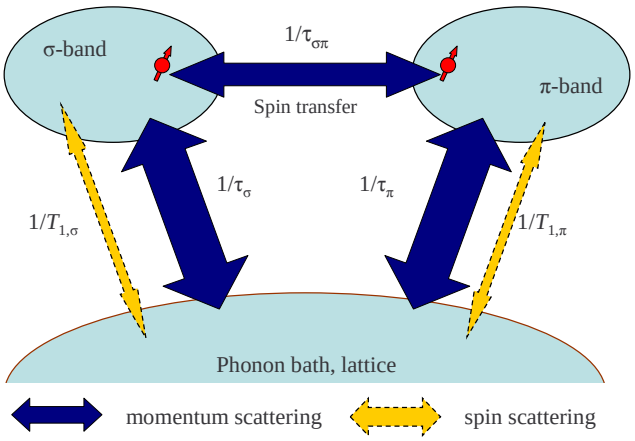

FIG. 2: (Color online) Schematics of the spin-lattice relaxation in MgB_2 in the two-band model framework. The arrow thicknesses represent the relaxation rates (not to scale). Note that the inter-band momentum scattering rate is larger than the spin-lattice relaxation rates, therefore there is a spin transfer between the two types of bands.

$$\frac{1}{T_1} = \frac{L_{\rm eff}^2}{\hbar^2}\frac{\tau}{1+\Delta\omega_{\rm eff}^2\tau^2}, \qquad (6)$$

This result returns the Elliott-relation when $\tau\Delta\omega_{\rm eff} \gg 1$ and gives a decreasing spin relaxation rate with increasing τ^{-1} when $\tau\Delta\omega_{\rm eff} \leq 1$, thus it can be regarded as a generalization of the Elliott-Yafet theory. In the following, we show that it describes the spin relaxation in MgB_2.

Electronic properties of MgB_2 are described by the so-called two-band model meaning that the conduction bands related to the boron σ and π bonds have different electron-phonon couplings, different affinity to defects, and that the inter-band momentum scattering is weaker than the intra-band ones [16]. As a result, the conductivity is given by a parallel resistor formula [16], i.e. the band with longer τ dominates the transport. In contrast, the CESR spin relaxation is dominated by the band with *shorter* T_1. Although the inter-band momentum scattering time, $\tau_{\sigma\pi}$ is longer than the intra-band momentum scattering times, τ_σ and τ_π, it is still much shorter than T_1. Thus an electron with a given spin state is scattered back and forth between the two types of bands several times before flipping its spin, which is depicted in Fig. 2. The overall $1/T_1$ is the average of the spin-lattice relaxation rates weighted by the relative DOS on the σ and π bands, $N_\pi = 0.56$ and $N_\sigma = 0.44$ [17]:

$$\frac{1}{T_1} = \frac{N_\pi}{T_{1,\pi}} + \frac{N_\sigma}{T_{1,\sigma}} \qquad (7)$$

In Fig. 3., we show the band structure of MgB_2 from Refs. [18, 19] near the Fermi energy. Two boron σ and

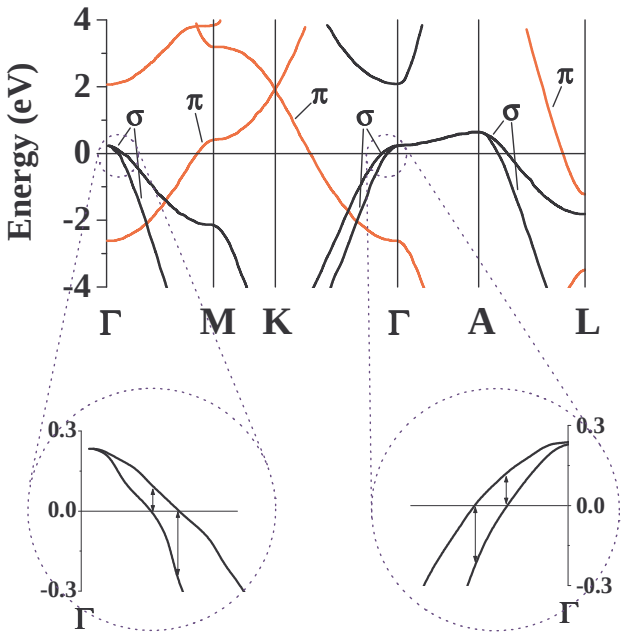

FIG. 3: (Color online). Band structure of MgB_2 near the Fermi energy after Refs. [18, 19]. Two of the σ bands (black) cross the Fermi surface near each other in the vicinity of the Γ and A points, whereas π bands (red) are separated from other bands with a larger optical gap at the crossing. We also show the dispersion with 8 times larger wave-vector resolution around the Γ points with vertical arrows for possible ΔE_σ values.

two π bands cross the Fermi energy such that the π bands are well separated from other bands with $\Delta E_\pi \geq 2$ eV whereas the two σ bands are close to each other and $\Delta E_\sigma \approx 0.2$ eV. Based on the above theory and Eq. 6., we conclude that T_1 follows the EY mechanism for the π bands, whereas it is described the by the novel mechanism for the σ bands. With this in mind and the two band model result of Eq. 7, we describe the CESR linewidth with:

$$\Delta B = \Delta B_0 + \frac{1}{\gamma\hbar^2}\left(\frac{N_\pi L_{{\rm eff},\pi}^2}{\Delta\omega_{{\rm eff},\pi}^2}\frac{1}{\tau_\pi} + \frac{N_\sigma L_{{\rm eff},\sigma}^2\tau_\sigma}{1+\Delta\omega_{{\rm eff},\sigma}^2\tau_\sigma^2}\right) \qquad (8)$$

where we introduced the band index for the parameters. The momentum relaxation times are calculated using the Debye-model and assuming clean samples, i.e. zero residual scattering:

$$\frac{1}{\tau_n} = \frac{2\pi {\rm k_B} T\lambda_{{\rm tr},n}}{\hbar}\int_0^{\omega_{\rm D}}\frac{d\Omega}{\Omega}\left(\frac{\Omega}{\omega_{\rm D}}\right)^4\left[\frac{\hbar\Omega/{\rm k_B}T}{\sinh\frac{\hbar\Omega}{2{\rm k_B}T}}\right]^2, \qquad (9)$$

where $n = \sigma, \pi$, $\omega_{\rm D}$ is the Debye frequency, and $\lambda_{{\rm tr},n}$ are the transport electron-phonon couplings from Ref. [16], which contain both intra- and inter-band scattering.

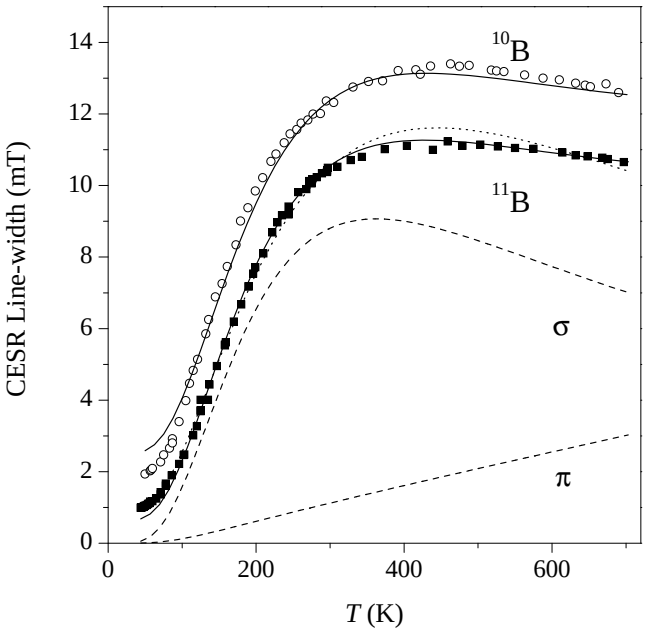

FIG. 4: Measured (symbols) and calculated (solid curves) CESR line-width in MgB_2 with ^{11}B and ^{10}B. Note the larger residual line-width in the latter sample. Dashed curves show the contributions to the line-width from the σ and π bands for the ^{11}B. Dotted curve shows a calculation for the the ^{11}B sample assuming $1/T_1$ is due to σ bands only.

In Fig. 4., we show the CESR line-width for $Mg^{11}B_2$ and $Mg^{10}B_2$ between 40 and 700 K and the calculated line-width using Eq. 8. with parameters in Table I. obtained from a fit. Results on the natural boron sample are identical to the data on the $Mg^{11}B_2$ within experimental error and are not shown. The larger residual line-width in the ^{10}B ($\Delta B_0 = 2$ mT) than in the ^{11}B sample ($\Delta B_0 = 1$ mT) is related to a larger defect concentration in the starting boron, the preparation method and the starting Mg being identical. Apart from this, the only difference between the two samples are the different Debye temperature, Θ_D. The calculated CESR line-width (solid curves) reproduces well the experimental data with the parameters in Table I. The dotted curve in Fig. 4. is a calculation assuming that relaxation is given by the σ bands alone, which accounts relatively well for the data with three free parameters (L_σ, $\Delta E_{\mathrm{eff},\sigma}$, and ΔB_0). However, it fails to reproduce the slope of ΔB at higher temperatures, which shows the need to include relaxation due to the π bands.

The determination of $\Delta E_{\mathrm{eff},\sigma} \approx 0.2$ eV is robust as it is given by the temperature where the maximal ΔB is attained and its value is close to values expected from the band structure (arrows in Fig. 3.). Knowledge of $\Delta E_{\mathrm{eff},\sigma}$ allows to determine the SO splitting independently, $L_{\mathrm{eff},\sigma} = 0.64$ meV, as usually only the $L/\Delta E$ ratio is known. The SO splitting for the atomic boron $2p$ orbital is $L = 0.23$ meV (Ref. [4]), which is in a reasonable agreement with the experimental value. ΔE_π was fixed to 2 eV which affects $L_{\mathrm{eff},\pi}$ as these are not independent.

TABLE I: Parameters used to calculate the CESR line-width in MgB_2. The given standard deviations indicate the free parameters of the fit.

λ_{tr} [16]		L_{eff} (meV)		ΔE_{eff} (eV)		Θ_D (K)	
σ	π	σ	π	σ	π	^{11}B	^{10}B
1.09	0.46	0.64(2)	2.8(1)	0.194(5)	2	535(15)	555(15)

The isotope effect on Θ_D is $^{10}\Theta_D/^{11}\Theta_D = 1.04$, that is close to the expected $\sqrt{11/10}$ ratio. The Θ_D values are in agreement with the 440..1050 K values in the literature, which scatter depending on the experimental method [20, 21]. We note that the model could be improved by including the Einstein model of phonons or by an exact treatment of the band structure dependent SO coupling [22], and band-band separation.

Finally, we note that the maximum of $1/T_1$ occurs when $\tau\Delta\omega \approx 1$. This coincides with the Ioffe-Regel criterion for the electron transport [23] when the band-band separation is comparable to the bandwidth, w, e.g. in narrow band metals. For MgB_2, $w \approx 10$ eV [18] therefore saturation of the CESR line-width is not accompanied by a saturation of electrical resistivity.

In conclusion, we explained the anomalous spin-lattice relaxation in MgB_2 by extending the Elliott-Yafet theory to the case of rapid momentum scattering and near lying bands. The anomaly does not occur in conventional metals, which have small electron-phonon coupling and well separated bands. A similar phenomenon, the so-called Dyakonov-Perel relaxation [1], occurs for semiconductors without inversion symmetry, although its physical origin is different. The band structure of some of the other diborides in e.g. BeB_2 and CaB_2 predicts [19] similar phenomena but conventional spin relaxation in AlB_2, ScB_2, and YB_2. We also predict that the described effect is sensitive to pressure since this shifts the σ bands [24].

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[1] I. Žutić, J. Fabian, and S. D. Sarma, Rev. Mod. Phys. **76**, 323 (2004).
[2] G. Fehér and A. F. Kip, Physical Review **98**, 337 (1955).
[3] R. J. Elliott, Phys. Rev. **96**, 266 (1954).
[4] Y. Yafet, Solid State Phys. **14**, 1 (1963).
[5] F. Beuneu and P. Monod, Phys. Rev. B **18**, 2422 (1978).
[6] L. Forró and F. Beuneu, Solid State Commun. **44**, 623 (1982).
[7] P. Petit, J. Robert, T. Yildirim, and J. E. Fischer, Phys. Rev. B **54**, 3764(R) (1996).
[8] F. Simon, A. Jánossy, T. Fehér, F. Murányi, S. Garaj, L. Forró, C. Petrovic, S. L. Bud'ko, G. Lapertot, V. Kogan, et al., Phys. Rev. Lett. **87**, 047002 (2001).
[9] F. J. Adrian, Phys. Rev. B **53**, 2206 (1996).
[10] F. Simon, F. Murányi, T. Fehér, A. Jánossy, L. Forró, C. Petrovic, S. L. Bud'ko, and P. C. Canfield, Phys. Rev. B **75**, 024519 (2007).
[11] P. Monod and M. Elsen, private communication.
[12] R. R. Urbano, P. G. Pagliuso, C. Rettori, Y. Kopelevich, N. O. Moreno, and J. L. Sarrao, Phys. Rev. Lett. **89**, 087602 (2002).
[13] H. Mori and K. Kawasaki, Prog. Theor. Phys. **27**, 529 (1962).
[14] M. Oshikawa and I. Affleck, Phys. Rev. B **65**, 134410 (2002).
[15] A. A. Abrikosov, L. P. Gor'kov, and I. E. Dzyaloshinski, *Methods of Quantum Field Theory in Statistical Physics* (Dover Publications, New York, 1963).
[16] I. I. Mazin, O. K. Andersen, O. Jepsen, O. V. Dolgov, J. Kortus, A. A. Golubov, A. B. Kuzmenko, and D. van der Marel, Phys. Rev. Lett. **89**, 107002 (2002).
[17] H. J. Choi, D. Roundy, H. Sun, M. L. Cohen, and S. G. Louie, Nature **418**, 758 (2002).
[18] J. Kortus, I. I. Mazin, K. D. Belashchenko, V. P. Antropov, and L. L. Boyer, Phys. Rev. Lett. **86**, 4656 (2001).
[19] N. I. Medvedeva, A. L. Ivanovskii, J. E. Medvedeva, and A. J. Freeman, Phys. Rev. B **64**, 020502(R) (2001).
[20] V. A. Gasparov, N. S. Sidorov, and M. P. Zver'kova, I. I. Kulakov, JETP Lett. **73**, 532 (2001).
[21] M. Putti, E. G. d'Agliano, D. Marre, F. Napoli, M. Tassisto, P. Manfrinetti, A. Palenzona, C. Rizzuto, and S. Massidda, Eur. Phys. J. B **25**, 439 (2002).
[22] J. Fabian and S. Das Sarma, Phys. Rev. Lett. **83**, 1211 (1999).
[23] O. Gunnarsson, Rev. Mod. Phys. **75**, 1085 (2003).
[24] K. Kobayashi and K. Yamamoto, J. Phys. Soc. Jap. **70**, 1861 (2001).